

Research Articles: Air Pollution

Absorption Cross-Sections of Atmospheric Constituents: NO₂, O₂, and H₂O

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Abstract

Absorption spectroscopy, which is widely used for concentration measurements of tropospheric and stratospheric compounds, requires precise values of the absorption cross-sections of the measured species. NO₂, O₂ and its collision-induced absorption spectrum, and H₂O absorption cross-sections have been measured at temperature and pressure conditions prevailing in the Earth's atmosphere. Corrections to the generally accepted analysis procedures used to resolve the convolution problem are also proposed.

Keywords: Absorption cross-section; air pollution measurement; convolution procedures; DOAS technique; Fourier transform spectrometer; NO₂, O₂, H₂O, collision-induced absorption; stratosphere; troposphere; UV, visible, near IR

1 Introduction

Absorption spectroscopy is a widely used technique for concentration measurements of tropospheric and stratospheric compounds. In the UV-visible region, this method is widely used for monitoring urban pollutants [1,2], e.g. ozone, nitrogen dioxide, benzene, toluene, and sulphur dioxide, and also for determining the amounts of trace constituents (e.g. OClO, BrO) in the stratosphere [3]. Furthermore, the absorption of atmospheric constituents is also required by the scientific community for the study of the transmission and radiative properties of the atmosphere where O₂ and H₂O play an important role [4,5]. Finally, some cloud properties can be deduced from the absorption bands of O₂ and its collision-induced spectrum [6,7]. In the case of UV measurements, absorption structures due to O₂ and NO₂ overlap the ozone

signature and need to be properly removed to allow the accurate determination of the ozone concentration.

As cross-sections depend on temperature and pressure, it is essential for these applications to simulate atmospheric conditions as closely as possible when measuring them in the laboratory.

A bad choice of the cross-section used when analysing the data can give rise to important errors. In the case of the stratospheric NO₂, if a cross-section which does not correspond to the stratospheric conditions is chosen, for example, errors as large as 20 % can occur on the column abundance [8].

As most of the field instruments using absorption spectroscopy use a rather low resolving power, the DOAS (Differential Optical Absorption Spectroscopy) procedure involves a convolution of the laboratory data with the appropriate instrumental function. Absorption cross-sections therefore have to be measured at high resolution in order to minimise convolution effects. It will be shown that great care has to be taken when convoluting the laboratory data. A common error is to convolve the cross-sections directly.

After a short description of the experimental set-up, we will present a synthesis of our results for NO₂, O₂ and H₂O absorption cross-sections in the UV, visible and near-IR regions. More details concerning these studies and a comparison between our results and previous findings will be discussed in forthcoming papers. The results of these measurements will be available on our web site (<http://www.oma.be/BIRA-IASB/>) or on request. Finally, some important considerations will be presented concerning the correct use and convolution of cross-sections.

2 Experimental

All the measurements were performed with a BRUKER IFS120M Fourier transform spectrometer (FTS) coupled to one of two multiple reflection absorption cells (\rightarrow Fig. 1). The BRUKER 120M FTS is characterised by a maximum resolution of 0.008 cm^{-1} and a resolving power better than 10^6 . It is capable of recording spectra from the MIR to the UV with a wave number accuracy of 5.10^{-3} cm^{-1} . A FTS combines the advantages of a great sensitivity and of a built-in wave number calibration. The latter advantage is achieved by the use of a He-Ne laser which allows the interferogram to be digitised at equal intervals. With the Fourier Transform Spectrometer used in this work, an accuracy of about 0.005 cm^{-1} ($8 \times 10^{-5}\text{ nm}$ at 400 nm) is achieved on the wave numbers.

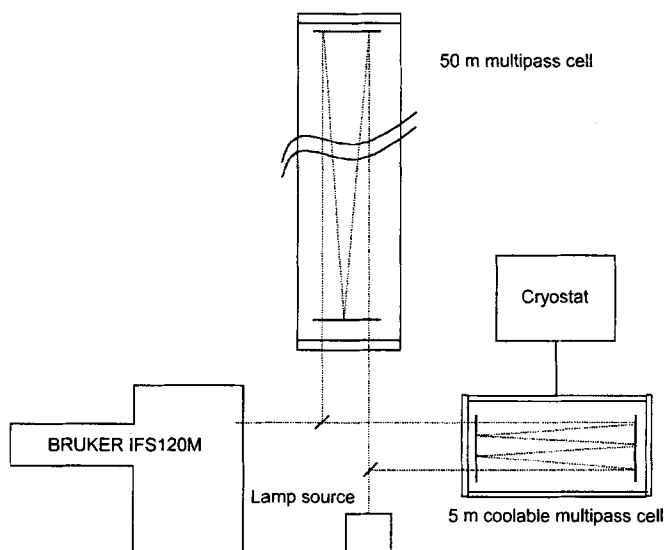


Fig. 1: Experimental set-up

For the 5 m cell [9], the temperature can be stabilised down to 220 K by a circulating cooling fluid. The total absorption path can be adjusted up to 300 m in the visible region. The temperature is measured by five platinum sensors distributed regularly inside the cell. The temperature variation from end to end never exceeds $\pm 0.2\text{ K}$ at 220 K.

The 50 m cell [10] is not temperature stabilised and optical paths can be attained up to a few kilometres in the visible spectrum. The temperature is monitored by three sensors placed at the extremities and in the middle of the cell.

The pressure is monitored by a MKS Baratron capacitance manometer with 1 torr, 10 torr, and 1000 torr full scale heads.

In this work, two light sources were used: A high pressure non-ozone-free xenon arc lamp (450 W) for the region extending from 42000 to 20000 cm^{-1} (238-500 nm), and a tungsten-halogen lamp (250 W) for the visible region below 20000 cm^{-1} ($\lambda > 500\text{ nm}$). UV-, GaP- and Si-diode detectors were used to cover the entire spectral region.

Table 1 summarises the experimental conditions used to record the different spectra.

The error budget was evaluated on the absorption cross-sections, taking into account the error on the pressure (1% full scale), the temperature ($< 0.2\%$), the absorption path length (0.5%), the impurities in the samples (2% for NO_2 , $< 0.1\%$ for O_2 and H_2O), and the absorbance. The uncertainty on the absorbance depends on the signal-to-noise ratio, which is a wave number dependent function of the detector noise, lamp evolution with time and absorption. In the case of NO_2 , the error budget includes error due to gas adsorption on the cell walls and to the uncertainty on the equilibrium constant between NO_2 and its dimer N_2O_4 . The total uncertainty on the cross-sections, which depends on the spectral region, varies from 1 to 4% for NO_2 at room temperature, 3 to 6% for NO_2 at 220K, 3 to 30% for O_2 in the UV region, and 2 to 50% for O_2 in the visible region. At high resolution, the uncertainty on the line intensities is 3 to 20% for O_2 , and 1 to 10% for H_2O .

3 Results and Discussion

3.1 NO_2

The NO_2 absorption cross-section was derived at 220 K and 294 K at a resolution of 2 cm^{-1} from a series of spectra recor-

Table 1: Experimental conditions used for the NO_2 , O_2 and H_2O measurements

	NO_2	O_2	H_2O
Cell base length (m)	5	5, 50	50
Absorption path length (m)	20, 60	60, 202, 402, 602, 1002	602
Spectral region (cm^{-1})	10000-42000	8000-42000	8000-30000
Lamp	Xe, W	Xe, W	Xe, W
Detector	UV vacuum, Si, GaP	UV vacuum, Si, GaP	UV vacuum, Si, GaP
Temperature (K)	220, 294	220, 287	287
Pressure range (torr)	0.007 to 2	20 to 750 (pure)	0.4, 1.1, 13.7 (pure)
		300 to 750 (20% O_2 , 80% N_2 or Ar)	125 to 600 (13.7 torr H_2O + N_2)
Resolution (cm^{-1})	2	0.02, 0.12, 2	0.03, 0.06
Recording time per experiment			
high resolution (hours)		10 - 24	12 - 24
low resolution (minutes)	30 - 60	50 - 60	

ded with pure NO_2 at pressures ranging from 0.007 to 2 torr. Spectra were recorded from 10000 cm^{-1} to 42000 cm^{-1} . The determination of the NO_2 cross-section is complicated by the presence of its dimer N_2O_4 , which must be considered in order to derive the correct partial pressure of NO_2 in the cell. Moreover N_2O_4 itself strongly absorbs in the UV region. The method of separation of the two contributions from a series of spectra obtained at different NO_2 partial pressures has already been described [11] and will not be repeated here. Figure 2 shows the NO_2 cross-section measured at 294 K for the entire spectral region. The total uncertainty is estimated to be on the order of 3% below 40000 cm^{-1} and reaches 6% between 42000 and 40000 cm^{-1} .

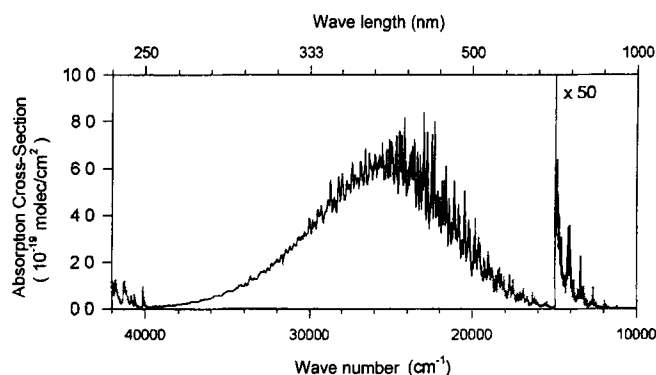


Fig. 2: Absorption cross-section of NO_2 at 294 K from 42000 to 10000 cm^{-1}

The cross-section obtained at 220 K shows similar structures, although with changes in the amplitude of the peaks. The absorption increases at the peak maxima and decreases at the peak minima when the temperature decreases. Such a dependence is expected since the population of the higher energy rotational levels increases when the temperature increases.

A significant pressure effect at both temperatures has been observed in the visible part of the spectrum. This effect seems to be restricted to some absorption bands located in the 12000 - 20000 cm^{-1} spectral range. A similar effect could not be detected in the 20000 - 25000 cm^{-1} region which is used for most of the atmospheric measurements.

3.2 O_2

O_2 absorption cross-sections have been determined from the UV to the visible spectra:

- In the UV, the O_2 Herzberg bands were recorded at high resolution (0.12 cm^{-1}) between 33000 and 42000 cm^{-1} .
- Also in the UV, low resolution (2 cm^{-1}) spectra were measured in order to separate the underlying continuum from the O_2 discrete structures.
- In the visible, low resolution spectra (2 cm^{-1}) were taken in order to determine the broadband O_2 collision induced,

absorption cross-section. The atmospheric bands of the O_2 b-X system were also recorded at high resolution (0.02 cm^{-1}).

3.2.1 High-resolution study of the Herzberg systems

FTS absorption spectra of oxygen have been obtained in the wave number region 33000 - 42000 cm^{-1} at high resolution (0.12 cm^{-1}) with absorption paths of 202 to 602 m and pressures ranging from 20 to 750 torr. Under these experimental conditions, the rotational lines of the three Herzberg systems ($A^3\Sigma_u^+ - X^3\Sigma_g^-, c^1\Sigma_u^- - X^3\Sigma_g^-, A'^3\Delta_u - X^3\Sigma_g^-$) are well resolved and superposed on collision-induced diffuse bands having a triplet structure and which progressively emerge as the pressure is increased (called the Wulf bands, see 3.2.2).

The rotational assignments of the Herzberg bands have been extended up to $N''=31$ in the most intense bands, thereby allowing the derivation of more accurate molecular constants. New vibrational levels ($v'=17, 18, 19$ of $c^1\Sigma_u^-$ and $v'=12$ of $A'^3\Delta_u$) are observed in the region close to the dissociation limit, where extensive perturbations, arising from interactions with $a^3\Pi_u$ state, affect the last levels of the three excited states A, c and A'.

The integrated intensities of the bands have been determined and their oscillator strengths are given in Table 2. For the A-X transition, they are in good agreement with those of previous works[12-16], but significant discrepancies with older literature data are found for the c-X and A'-X systems.

The line parameters of the Herzberg bands were used to isolate the contribution of the Wulf bands from the overall spectrum (see below).

3.2.2 The Wulf bands

With increasing pressure, diffuse bands with a triplet structure appear in the UV region and overlap the Herzberg bands (\rightarrow Fig. 3.a and Fig. 4.a). These bands were observed in 1928 by Wulf [17], and have since been reported by several authors [18,19]. The nature of the Wulf bands whose intensity is proportional to the square of the pressure is still controversial: They are attributed either to the O_4 dimer, to the $(\text{O}_2)_2$ collision complex or to collision-induced absorption (CIA) [19-22].

Spectra recorded here at a given O_2 pressure with various pressures of N_2 and Ar show that the intensity of the Wulf bands depends on the total pressure, and that, in the present range of pressure, the Wulf bands have the same features and the same strength, whatever the collisional partner. This can be seen in Figure 3 where the absorption cross-section of pure O_2 at 300 torr (\rightarrow Fig. 3.a) is compared to the cross-section obtained at the same total pressure but with 60 torr of O_2 and 240 torr of N_2 (\rightarrow Fig. 3.b). Fig. 3.c shows the result of the subtraction of the two upper spectra. In spite of

Table 2: Oscillator strengths for the O₂ Herzberg bands (units: 10⁻¹²)

v'-v''	A - X bands				b - X bands			A' - X bands			
	This work	Y	HN	H	This work	B	H	This work	B	H	KW
0-0	0.1			0.1							
1-0	0.8			0.9							
2-0	3.7			3.9	0.1			0.4			
3-0	11.0			11.4	0.2			1.2			
4-0	25.0	24.3	30.0	26.6	0.5			2.7			
5-0	51.2	49.8	53.8	51.4	1.0			5.2			5.9
6-0	83.5	82.8	79.8	85.8	1.7			8.7	30.2	8.4	
7-0	121.7	122.0	124.0	124.0	2.5			12.2	44.9	12.5	4.8
8-0	156.0	155.0	139.0	160.0	3.5			15.8	62.8	16.4	
9-0	175.7	171.0	140.0	178.0	4.6			17.6	76.2	19.2	7.4
10-0	166.0	164.0	120.0	168.0	5.3	1.8	3.9	17.9	83.9	20.2	
11-0	92.1	79.8	100.0	99.3	6.3	2.1	4.8	13.7	80.8	16.7	
12-0					6.9	2.4	5.7	7.0			
13-0					6.4	2.5	6.4				
14-0					6.8	2.5	7.1				
15-0					6.7	2.4	7.6				
16-0					5.1	2.4	7.9				
17-0					4.1						
18-0					2.3						
19-0					1.0						

Y = YOSHINO et al. (1995)
 HN = HASSON and NICHOLLS (1971)
 H = HUESTIS et al. (1994)
 B = BATES (1989)
 KW = KERR and WATSON (1986)

the presence of residuals from the discrete bands due to the saturation of the O₂ lines, it can clearly be seen that the underlying triplet structures have cancelled out perfectly. The same result is obtained by replacing N₂ by Ar. These experiments are strong evidence for attributing the Wulf bands to collision-induced absorption in O₂ and not to O₂-O₂ interactions. Indeed, both CIA and dimer absorption will show a quadratic dependence on the oxygen pressure in a pure sample, although only CIA will be influenced by the presence of a foreign gas (see a detailed discussion in ref. [23]).

In this work, measurements of spectra at various O₂ pressures (from 75 to 750 torr) from which the contribution of the Herzberg bands is subtracted by using the line parameters derived from the high resolution study (section 3.2.1) have allowed a calculation of the intensity of the Wulf bands.

Figure 4 shows the result of such a procedure. A O₂ spectrum recorded at 750 torr (→ Fig. 4.a) is separated into its three components: The Wulf bands (→ Fig. 4.c), the discrete lines of the Herzberg systems (→ Fig. 4.e), and the Herzberg continuum (→ Fig. 4.b). The detailed procedure will be described in a forthcoming paper. The CIA spectrum has also been modelled using the procedure described by Tabisz et al. [24]. The result of the use of this model is compared to the measured spectrum in Fig. 4.d and shows that the Wulf band system is thus adequately reproduced up to the dissociation limit.

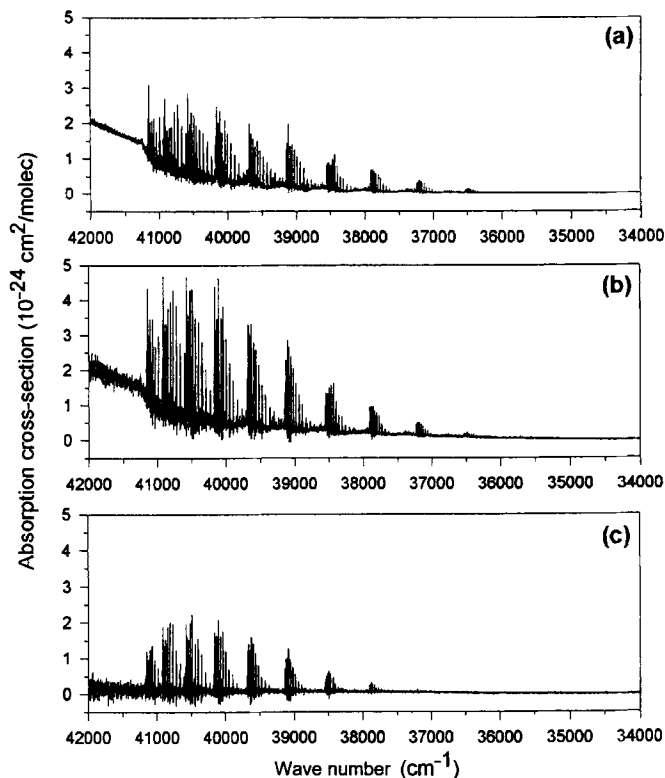


Fig. 3: Comparison of the pressure effects in pure O₂ and in mixtures of O₂ and N₂. Absorption cross-section of pure O₂ at 300 torr (a). Absorption cross-section of O₂ at 60 torr in the presence of 240 torr of N₂ (b). (c) is the difference between (a) and (b)

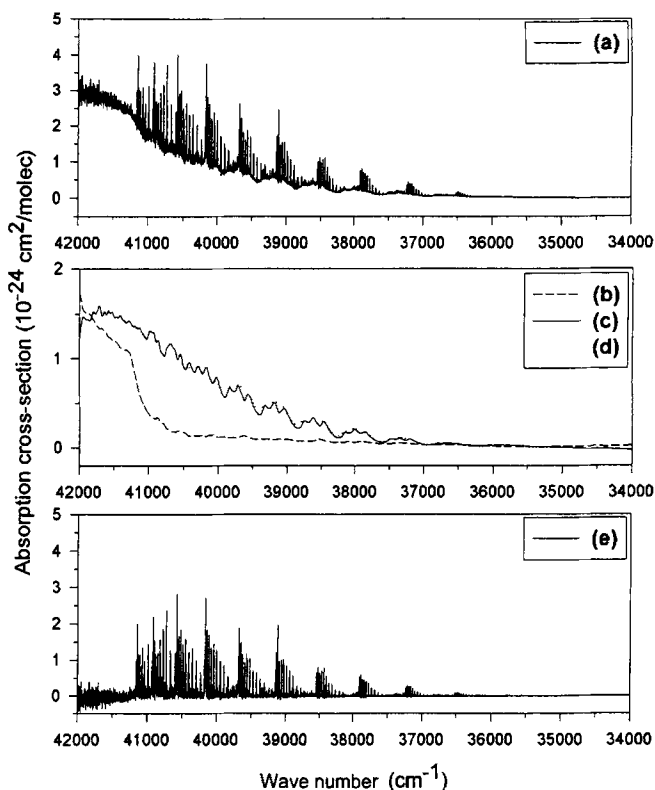


Fig. 4: The three components of an absorption spectrum of O_2 at 750 torr (a): The Herzberg continuum (b), the diffuse Wulf bands (c) and the discrete Herzberg bands (e). A model calculation of the Wulf bands is also shown in (d)

3.2.3 Visible absorption bands of O_2 and $(O_2)_2$

Many studies [25-29] have been reported on the collision absorption bands of O_2 lying in the visible and near UV regions. Recently, these bands attributed to the $(O_2)_2$ collision complex were observed in the atmosphere [30,31]. Laboratory spectra at 55 atm have also been reported by Greenblatt et al. [32].

In this work, laboratory absorption measurements were performed in these regions using the 50 m cell which allowed us to obtain absorption lengths of 1 km with relatively low pressure conditions (from 300 torr to 1 atm).

Comparisons between data of the present study and those at higher pressure obtained by Greenblatt et al. are presented

in Table 3. This table shows that the positions of the $(O_2)_2$ bands (band centres) measured in this study are slightly shifted in comparison to Greenblatt's measurements. The cross-sections determined in the present work are also larger by a few percent, whereas the bandwidths at half maximum are smaller by a few percent. This pressure dependence, however, although small, should be taken into account when analysing atmospheric spectra [33].

Figure 5 shows the band located at 15.889 cm^{-1} and the absorbance of the $(O_2)_2$ band when the contribution of the $b^1\Sigma_g^+(v'=2) - x^3\Sigma_g^-(v=0)$ band of O_2 (or atmospheric band) is subtracted.

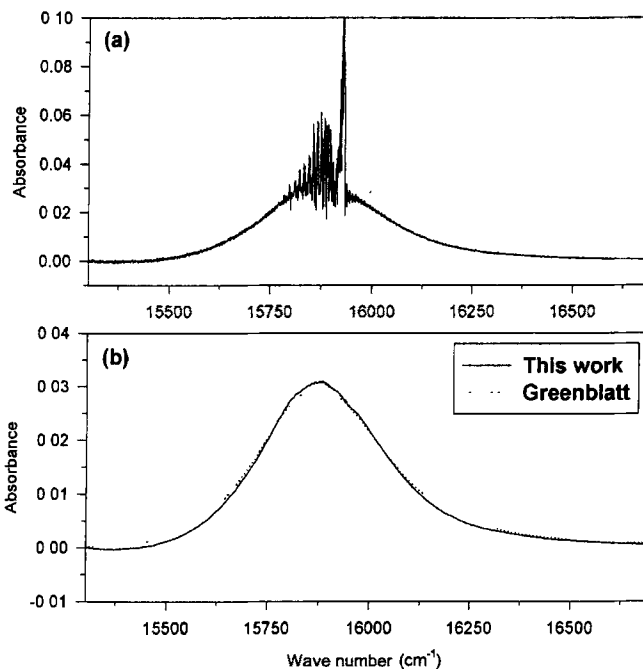


Fig. 5: (a) Observed spectrum: O_2 γ band superposed on the $(O_2)_2$ collision complex band. (b) $(O_2)_2$ collision complex band (obtained after subtraction of the γ band) compared to Greenblatt's data

The following method was used to remove the band contribution and will be detailed in a forthcoming paper: Using the data of a spectrum recorded at a resolution of 0.02 cm^{-1} (which allows a good characterization of the lines), a synthetic spec-

Table 3: Band centre positions, collision pair absorption cross-sections and bandwidths of the $(O_2)_2$ bands

Wave number (cm ⁻¹)		Collision absorption cross-section (10 ²⁶ cm ² /molecule ²)		FWHM (cm ⁻¹)	
This work	GREENBLATT et al.	This work	GREENBLATT et al.	This work	GREENBLATT et al.
29070	29121	1.2	1.2	328	356
27718	27739	4.3	4.1	336	369
26307	26302	2.5	2.4	287	304
22410	22386	0.6	0.6	260	281
20967	20951	6.6	6.3	244	272
18814	18790	1.1	1.0	335	360
17355	17325	12.0	11.0	353	348
15889	15873	7.6	7.2	324	348

trum is calculated at a resolution of 2 cm^{-1} and then subtracted from the observed spectrum to obtain the $(\text{O}_2)_2$ collision complex band.

3.3 H₂O vapour

The absorption spectrum of water vapour at room temperature was recorded at high resolution from the near IR to the UV ($8000\text{--}30000\text{ cm}^{-1}$). Spectra of pure H₂O at several pressures, as well as spectra with increasing pressures of N₂ were recorded in order to study the pressure dependence of the absorption lines. The experimental conditions are given in Table 1.

In addition, spectra of D₂O + HDO mixtures were recorded in the same conditions. Figure 6.a presents the visible part of the spectrum (Si-diode) and Figure 6.b an enlargement of a small portion around 16890 cm^{-1} . The latter shows a very good signal-to-noise ratio (~ 3000). The analysis of these spectra is currently under way.

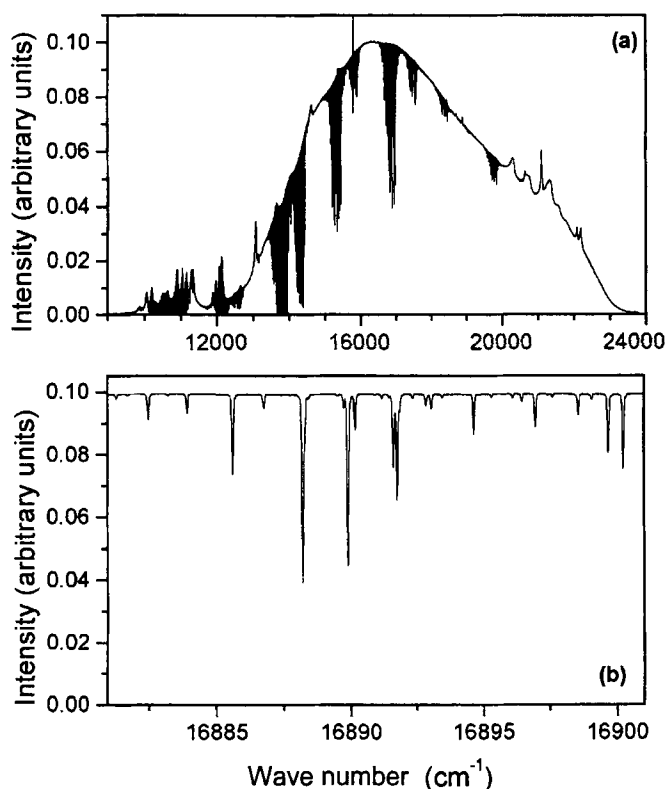


Fig. 6: (a) H₂O spectrum recorded at high resolution between 24000 and 10000 cm⁻¹. (b) Enlargement in the region from 16900-16880 cm⁻¹

4 Remarks on the Use of Cross-Sections in Atmospheric Studies

Absorption cross-sections of target species are used in atmospheric studies to measure their concentration. To derive concentrations, absorption cross-sections are compared, either

directly or through a differential form (as in the DOAS technique) to an experimental spectrum. A problem arises when laboratory spectra and field spectra have not been recorded at the same resolution. The common solution to this problem is to convolve the cross-sections by the instrumental function of the spectrometer used for the atmospheric experiments. The cross-sections are then believed to have been adapted to the resolution of the spectrometer. Various convolution techniques exist. Some of them even take into account the fact that the resolution of a grating spectrometer is not constant on the whole recorded interval [34]. However, these techniques introduce errors which can impair the precision on the retrieved concentrations.

The main error comes from the fact that the convolution is most often made on the spectrum or on the cross-section, and not on the absorbance ($A(\lambda)$) which is defined by the following expression:

$$A(\lambda) = \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = n\sigma(\lambda)d \quad (1)$$

In this formula, I and I_0 are spectra recorded with and without the sample, n is the concentration of the gas, d is the absorption path length and σ is the absorption cross-section.

Convoluting the cross-sections directly supposes that the logarithm function appearing in (1) and the convolution function commute, i.e. these two operations can be applied in any order. This is, of course, not the case. The usual procedure of comparing the absorbance of the atmospheric spectrum with convoluted differential cross-sections leads to an absorbance scale which is not linear in concentration, as is illustrated in Figure 7.

In part (a) of the figure, the correct absorbances of two lines having a 2:1 intensity ratio are presented. The resolution used to record these lines is twice smaller than the actual line width. Cross sections measured at a resolution five times greater than the line width are plotted in part (b) of Fig. 7 for different (path length \times pressure) products. It can easily be seen that the 2:1 intensity ratio progressively disappears when the path length \times pressure product increases. From this figure, it can also be inferred that, if one uses a single reference spectrum defined at the same resolution, the derived concentration of the sample will not be exact. Measurements are more accurate with low absorbance than with high absorbance. For low absorbance values, in fact, the calculated concentrations will be slightly higher than they should be, and they will be lower at high absorbance values. When recording spectra with a resolution higher than the line width, precise quantitative analysis requires the use of multiple reference spectra. Another solution is to use a calibration curve to correct the retrieved concentrations [35,36]. This calibration curve has to be evaluated regularly because of the changes with time of the instrumental function of the spectrograph. Of course, this problem does not arise if the width of the instrumental function is smaller than the width of the structures of the absorbing species. Unfortunately this is not the case with the grating spectrograph based DOAS systems, which usually work at fairly low resolution, and certainly not for molecules presenting very sharp features like O₂, benzene or toluene.

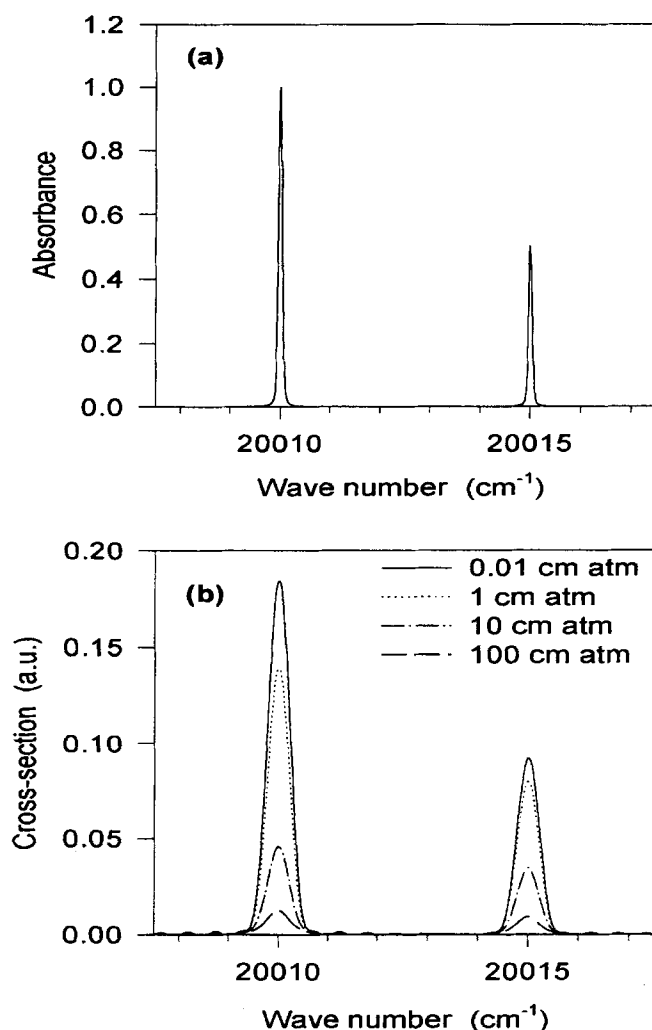


Fig. 7: Influence of resolution. Correct absorbance values for a pair of lines with a 2:1 intensity ratio (a) when the experimental resolution is half as small as the actual width of the lines. (b) Measured cross sections when the resolution is five times greater than the actual line width, for different path \times pressure products

The solution to this problem is to use a synthetic spectrum calculated at high resolution from precise absolute cross-sections [37] and to then convolute it to the desired resolution. Differential cross-sections are then obtained by filtering this synthetic spectrum instead of filtering the absolute cross-sections. This eliminates the non-linearities and the use of a calibration curve.

Fig. 7 also shows that laboratory spectra need to be recorded at a high enough resolution so that all the absorption features are fully resolved. This is again in contradiction with the common belief that cross-sections used in atmospheric studies need to be obtained imperatively with the same instrument as the one used for recording the atmospheric measurements.

Moreover cross-sections used in atmospheric studies should be recorded under pressure and temperature conditions as close as possible to those prevailing in the part of the atmosphere studied. A recent study of the NO₂ cross-sections [11]

has shown that the use of cross-sections obtained at room temperature for the colder stratosphere can lead to an over-estimation of the NO₂ amount by as much as 20%. In the same study, an important pressure effect was also mentioned for these cross-sections.

5 Conclusions

Absorption cross-sections and line parameters have been obtained for the O₂ and H₂O molecules from the UV to the visible and near IR. For the oxygen molecule, the analysis of the three Herzberg systems has been extended to several new vibrational bands. Integrated intensities and oscillator strengths have been obtained for the three systems. The study of the pressure dependency in the UV part of the spectrum has led to the separation of the O₂ Herzberg bands, the Herzberg continuum, and the Wulf bands. Experiments carried out with mixtures of several different gases demonstrate that the Wulf bands are caused by collision induced absorption (CIA). In the visible region, low resolution spectra have been recorded in order to determine the collision pair (O₂)₂ cross-section and the line parameters of oxygen atmospheric bands (A, B and γ).

Spectra of H₂O and isotopic mixtures of HDO and D₂O have been recorded from the near-IR to the UV at high resolution (0.03 and 0.06 cm⁻¹), at room temperature, and at various pressures. Analysis of these results is in progress.

If concentrations are to be obtained with a good accuracy in atmospheric studies, we have also shown that it is necessary to use laboratory cross-sections measured at high resolution. Moreover, the filtering process should be applied to a high-resolution synthetic spectra calculated with the absolute cross-section and convolved to the desired resolution, and not directly to the convolved cross-sections themselves. Furthermore, the pressure, concentration and temperature of the cross-section measurements must be as close as possible to the atmospheric conditions.

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